

PATENT

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OF

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FOR

REACTIVE COMPOSITIONS AND THEIR USE IN PAPER PRODUCTS

## **REACTIVE COMPOSITIONS AND THEIR USE IN PAPER PRODUCTS**

### **Background of the Invention**

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In the manufacture of paper products, such as facial tissue, bath tissue, paper towels, dinner napkins and the like, a wide variety of product properties are imparted to the final product through the use of chemical additives. Examples of such additives include debonders, wet strength agents, dry strength agents, sizing agents, opacifiers and the like. Unfortunately, when steps are taken to increase one property of the product, other characteristics of the product are sometimes adversely affected.

For instance, strength is typically increased by the addition of certain strength agent to the product. Although the strength of the paper product is increased by such strength agents, the resulting paper product may not always be soft. As a result, various chemical compositions can be applied to the paper product to reduce fiber bonding within the paper product and thereby increase softness.

Nevertheless, by reducing fiber bonding with a composition, the strength of the paper product is also reduced. For example, softening compositions can break various hydrogen bonds between adjacent fibers to increase the softness of the paper product. However, such debonding can often leave the fibers with little or no bonding capability, often resulting in loosely bound fibers that can extend from the surface of the resulting paper product. During processing and/or use, these loosely bound fibers can be freed from the paper product, thereby creating lint. Similarly, papermaking processes may also create zones of fibers that are poorly bound to each other but not to adjacent zones of fibers. As a result, during use, certain shear forces can liberate the weakly bound zones from the remaining fibers, thereby resulting in slough, i.e., bundles

or pills on surfaces, such as skin or fabric.

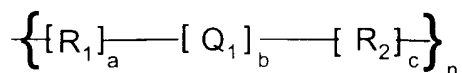
As a result, most paper products can only accommodate limited amounts of a softening composition. Moreover, even when applied at such limited amounts, the use of such a softening composition can still result in a much weaker paper product due, for example, to the lack of inter-fiber bonding capability remaining between the softened fibers.

Besides softening compositions, other compositions also present problems similar to those described above. For example, humectants are often applied to a paper web to increase its affinity for water. However, similar to a softening composition, a paper web may only be able to accommodate a limited amount of the humectant due to the limited number of available bonding sites.

As such, a need currently exists for a paper product that can be applied with a composition without severely impairing the bonding capability of the fibers so that certain characteristics such as strength, absorbency, lint production, slough, etc., are not substantially increased.

### **Summary of the Invention**

In accordance with one embodiment of the present invention, a paper product is provided that contains at least one paper web applied with a reactive composition having the following structure:



wherein,

$a, b, c > 0$ ;

$n \geq 1$ ;

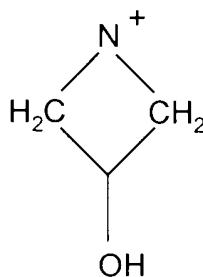
$R_1$  and  $R_2$  are monomers, homopolymers, or block or graft interpolymers that are capable of degrading interfiber hydrogen bonds contained within the paper web. For example, in one embodiment, at

least one of the  $R_1$  and  $R_2$  groups contain a  $C_8$  or higher aliphatic hydrocarbon moiety. Moreover, in some embodiments,  $R_1$  and/or  $R_2$  are of the form  $R_1-Z_1$  or  $R_2-Z_2$ , wherein  $Z_1$  and  $Z_2$  are bridging radicals selected from the group consisting of  $-CH_2-$ ,  $-COO-$ ,  $-CONR-$ ,  $-O-$ ,  $-S-$ ,  $-OSO_2O-$ ,  $-CONHCO-$ ,  $-CONHCHOHCHOO-$ , and combinations thereof.

$Q_1$  is a monomer, homopolymer, or block or graft interpolymer that contains:

i) a charged group (e.g., a positively charged atom) that is capable of forming an ionic bond with a charged group present on a first cellulosic fiber; and

ii) a pendant functional group that is capable of forming a covalent bond with a free reactive group present on a second cellulosic fiber. The covalent bonding functionality of the  $Q_1$  moiety can, in some embodiments, be provided by a group selected from epoxides, anhydrides, azetidiniums, or aldehydes. For example, in one embodiment, the  $Q_1$  moiety is an azetidinium ring having the following structure:

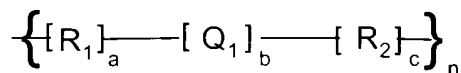


In general, the treated paper web may be single or multi-layered. For example, in one embodiment, a multi-paper web can be formed such that the first cellulosic fiber bonded to the charged group of the reactive composition is present within one of the layers and the second cellulosic fiber bonded to the covalent bonding functionality of the reactive

composition is present within another layer.

In addition, in some embodiments, the treated paper web can be incorporated into a multi-ply paper product. For example, in one embodiment, a multi-ply paper product can be formed such that the first cellulosic fiber bonded to the charged group of the reactive composition is present within one of the plies and the second cellulosic fiber bonded to the covalent bonding functionality of the reactive composition is present within another ply.

In accordance with another embodiment of the present invention, a method for forming a paper web that comprises providing a furnish of cellulosic fibers, depositing the furnish onto a foraminous surface to form a paper web, applying a reactive composition to the furnish of cellulosic fibers and/or the paper web, and thereafter, at least partially drying the paper web. The reactive composition has the following structure:



wherein,

$a, b, c > 0$ ;

$n \geq 1$ ;

$R_1$  and  $R_2$  are monomers, homopolymers, or block or graft interpolymers that are capable of imparting a certain function to the paper web. For example, in some embodiments,  $R_1$  and  $R_2$  can include a moiety selected from the group consisting of a polysiloxane, an aliphatic hydrocarbon, an amphiphilic hydrocarbon, and combinations thereof. In one particular embodiment, at least one of the  $R_1$  and  $R_2$  groups contains a  $C_8$  or higher aliphatic hydrocarbon moiety.

$Q_1$  is a monomer, homopolymer, or block or graft interpolymers that contains:

a) a positively charged atom that is capable of forming an ionic bond with a negatively charged group present on a first cellulosic fiber of the paper web; and

b) a pendant functional group that is capable of forming a covalent bond with a free reactive group present on a second cellulosic fiber of the paper web.

Other features and aspects of the present invention are provided in greater detail below.

### **Brief Description of the Drawings**

A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, which makes reference to the appended figures in which:

Fig. 1 illustrates one embodiment a method for forming a paper web in accordance with one embodiment of the present invention.

Repeat use of reference characters in the present specification and drawings is intended to represent same or analogous features or elements of the invention.

### **Detailed Description of Representative Embodiments**

Reference now will be made in detail to various embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their

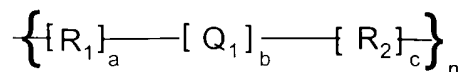
equivalents.

In general, the present invention is directed to a reactive composition that can be applied to a paper web containing cellulosic fibers without substantially impairing certain characteristics of the web. In particular, the reactive composition includes one or more moieties that are capable of imparting a certain property to the web (e.g., softening), a charged group (e.g., a positively charged atom), and a pendant functional group that is capable of forming a covalent bond with a cellulosic fiber. For example, in one embodiment, the reactive composition includes aliphatic hydrocarbons that debond the cellulosic fibers within the web, thereby softening the web. Further, in one embodiment, the reactive composition also includes a pendant hydroxyl group that is capable of covalently bonding to a carboxyl group of a cellulosic fiber.

Due to its particular structure, the reactive composition of the present invention can retain its charge even after the formation of the covalent bond between the pendant group and a cellulosic fiber. This retained charge can allow for, among other possibilities, multiple attachment between debonded fibers within the same or a different paper web. Thus, when the reactive composition contains one or more softening functionalities, such multiple fiber attachments can further inhibit the creation of lint and slough.

In general, the reactive composition of the present invention has a structure as set forth below in Formula 1:

(1)



wherein,

$a, b, c > 0$ ;

$n \geq 1$ ; and

$R_1$  and  $R_2$  are monomers, homopolymers, or block or graft  
interpolymers that are capable of imparting some functional property to  
the paper web when applied thereto.  $R_1$  can also take the form of  $R_1-Z_1$   
and  $R_2$  can take the form of  $Z_2-R_2$  where  $Z_1$  and  $Z_2$  are any bridging  
radicals, the same or different, that are capable of attaching the functional  
groups  $R_1$  and  $R_2$  to  $Q_1$ , respectively. For example, some suitable  
bridging radicals that can be utilized for  $Z_1$  and/or  $Z_2$  include, but are not  
limited to,  $-CH_2-$ ,  $-COO-$ ,  $-CONR-$ ,  $-O-$ ,  $-S-$ ,  $-OSO_2O-$ ,  $-CONHCO-$ ,  $-$   
 $CONHCHOHCHOO-$ , and the like.

In general, the  $R_1$  and  $R_2$  functional groups of Formula 1 can have  
a variety of different structures to impart a variety of different  
characteristics to a web when applied thereto. For example, in one  
embodiment,  $R_1$  and/or  $R_2$  can be monomer units or block or graft  
copolymer that act as humectants (i.e., a material that has an affinity for  
water) to enhance the absorption capabilities of the paper web.

In addition,  $R_1$  and/or  $R_2$  can also be a monomer, homopolymer, or  
block or graft interpolymers, that functions to provide some softening affect  
to a paper web by debonding interfiber hydrogen bonds contained within  
the paper web. For instance, some examples of suitable functional  
groups that can provide a softening affect to a paper web include, but are  
not limited to, quaternary ammonium groups, imidazolinium groups,  
bisimidazolinium groups, diquaternary ammonium groups, polyquaternary  
ammonium groups, phospholipid derivative groups, fatty and carboxylic  
acid derivative groups, and mono- and polysaccharide derivatives. Other  
suitable functional groups can include polysiloxanes (e.g., polydimethyl  
siloxanes), aliphatic hydrocarbons, amphiphilic hydrocarbons, etc. In one  
particular embodiment,  $R_1$  and/or  $R_2$  can be a monomer, homopolymer, or



a block or graft interpolmer containing a C<sub>8</sub> or higher linear or branched, saturated or unsaturated, substituted or unsubstituted aliphatic hydrocarbon moiety. Still other suitable materials that can provide a softening affect are disclosed in U.S. Patent Nos. 5,529,665 to Kaun and 5,558,873 to Funk, et al., which are incorporated herein in their entirety by reference thereto for all purposes.

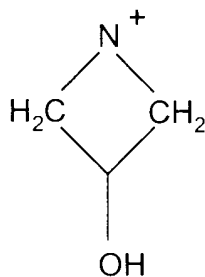
In one embodiment of the present invention, one or both of the functional groups R<sub>1</sub> and R<sub>2</sub> function to debond the cellulosic fibers within a web to soften the web. Unfortunately, the use of even small amounts of a softening moiety in a paper web can sometimes lead to excessive degradation of the web surface(s), thereby resulting in significant increases in slough and lint production. This degradation is believed to be at least partially due to the propensity of the softening moieties to break hydrogen bonds between adjacent fibers, thereby leaving loosely bonded fibers extending from the surface of the web. During further processing and/or use, these loosely bonded fibers can come free of the paper product. Thus, although a softening moiety can provide a soft, lubricated surface feel, it can also cause surface degradation by lessening the ability of the fibers to remain on the web surface.

Thus, in accordance with the present invention, the reactive composition also includes a functional group possessing a covalent bonding capability and a charged group to allow better interfiber bonding of the softened fibers within the web. For example, referring again to Formula 1, one particular embodiment of the reactive composition of the present invention contains a moiety, Q<sub>1</sub>, which is a monomer, homopolymer, or block or graft interpolmer that contains:

- i) a charged group, in particular, a positively charged group; and
- ii) a pendant functional group capable of forming a covalent bond with a reactive group contained on a cellulosic fiber.

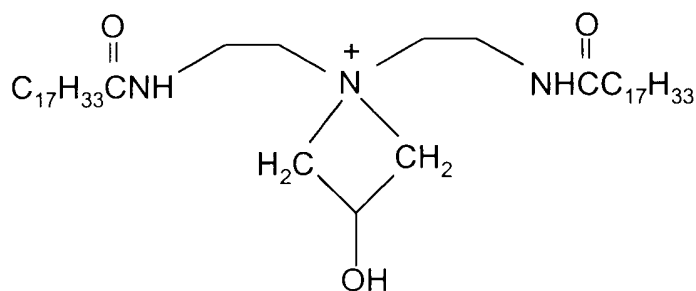
For instance, in one embodiment, the pendant functional group of the  $Q_1$  moiety forms a covalent bond with a certain free reactive group present on a cellulosic fiber. However, because the reactive composition of the present invention contains a charged group that is separate from the pendant functional group, the  $Q_1$  moiety, as indicated above, still possesses some charge. This remaining charge can be useful for a variety of reasons. For example, in some embodiments, the remaining charged group can possess a positive charge for forming an ionic bond with certain negatively charged groups present on another cellulosic fiber. Consequently, the reactive composition of the present invention can possess at least two bonding sites for bonding together multiple cellulosic fibers.

For example, in some embodiments, the pendant functional group of the  $Q_1$  moiety can be provided by a group selected from epoxides, anhydrides, azetidiniums, aldehydes, and the like. In one particular embodiment, the  $Q_1$  moiety can contain an azetidinium group having the following structure:

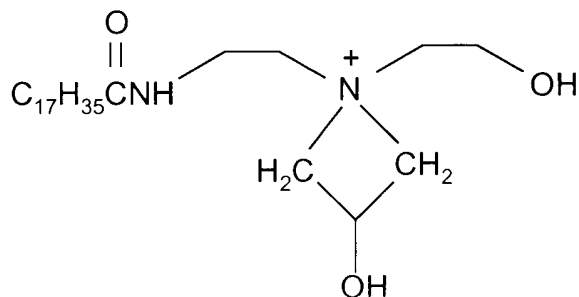


Two embodiments of reactive compositions of the present invention that contain an azetidinium ring structure as the  $Q_1$  moiety and also contain a long chain alkyl group softening moiety as the  $R_1$  and  $R_2$  groups for softening the web are set forth below as Formulas 3 and 4:

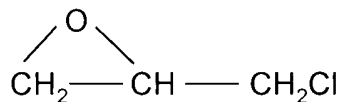
(3)



(4)

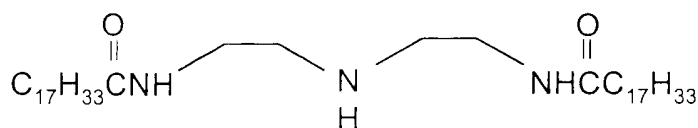


In some embodiments, the reactive compositions of Formulas 3 and 4 can be prepared by reacting a known reactant, such as a long chain alkyl group softening moiety with epichlorohydrin, which has the following structure:

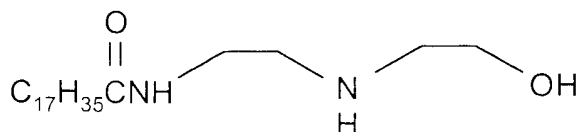


Specifically, the softening group reactants that can be utilized are set forth below in Formulas 5 and 6, respectively:

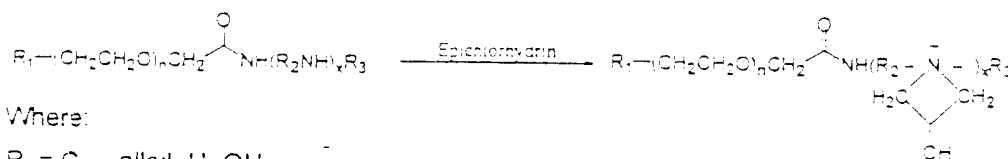
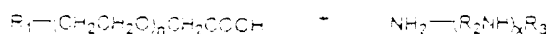
(5)



(6)



In addition, one embodiment of a method for forming a reactive composition that contains an azetidinium ring structure as the  $Q_1$  moiety and also contains a polyethylene glycol softening moiety as the  $R_1$  and  $R_2$  groups is set forth below as Formula 7:



Where:

 $R_1 = \text{C}_{1-30}$  alkyl, H, OH $R_2 = (\text{CH}_2)_m$  where  $m \geq 1$  $x \geq 1$  $n \geq 1$  $R_3 = \text{alkyl}, \text{CH}_2\text{CH}_2\text{OH}, \text{CH}_2\text{CH}_2\text{NH}_2$ 

In the embodiments shown above, the azetidinium ring structure contains both the charged group and the pendant functional group of the  $Q_1$  moiety. In particular, the pendant hydroxy group of the azetidinium group can form a covalent bond with certain free reactive groups that are present are on a cellulosic fiber either naturally or by the addition of chemical additives. In addition, even after the covalent bond is formed,

the azetidinium ring structure retains a separate, positively charged nitrogen atom that can form an ionic bond with certain negatively charged groups present on another cellulosic fibers, such as carboxyl or aldehyde groups. It should also be understood that, besides nitrogen, other positively charged groups (e.g., single or multiple atoms) can also be utilized in the present invention.

As stated above, a variety of free reactive groups can be present on a cellulosic fiber, either before or after pulping or web formation, to form a covalent bond with the pendant functional group of the reactive composition of the present invention. For example, the free reactive group present on the cellulosic fiber may be a carboxyl group. Further, other free reactive groups formed on the cellulosic fibers by the addition of a chemical additive can be utilized. Some examples of such free reactive groups include, but are not limited to, other carboxyl groups (e.g., formed by the addition of carboxymethyl cellulose), aldehyde groups (e.g., formed by the addition of hydrolytic enzymes), or primary and secondary amines (e.g., formed by the addition of wet or dry strength agents).

In general, the reactive composition of the present invention can be incorporated into a paper product to enhance certain characteristics of the product. As used herein, a "paper product" generally refers to various products, such as facial tissue, bath tissue, paper towels, and the like. A paper product of the present invention can generally be produced from a paper web having one or multiple layers. Moreover, depending on the desired characteristics of the paper product, it can contain multiple paper webs (i.e., plies) so that the paper product is a single- or multi-ply product. In one embodiment, for example, a three-ply paper product can contain two plies containing a composition of the present invention. Normally, the basis weight of a paper product of the present invention is less than about 120 grams per square meter (gsm), in some embodiments

less than about 70 grams per square meter, and in some embodiments, between about 10 to about 50 gsm.

Regardless of the overall structure of the paper product, any of a variety of materials can be used to form the paper product. For example, the material used to make a paper product of the present invention can include pulp fibers either alone or in combination with other types of fibers. The pulp fibers may be softwood fibers having an average fiber length of greater than 1 mm and particularly from about 2 to 5 mm based on a length-weighted average. Such fibers can include northern softwood kraft, southern softwood kraft, redwood, red cedar, hemlock, pine (e.g. southern pines), spruce (e.g. black spruce), combinations thereof, and the like. Exemplary commercially available pulp fibers suitable for the present invention include those available from Kimberly-Clark Corporation under the trade designations "Longlac-19". Hardwood fibers, such as eucalyptus, maple, birch, aspen, and the like, can also be used. Moreover, secondary fibers obtained from recycled materials may be used, such as fiber pulp from sources such as, for example, newsprint, reclaimed paperboard, and office waste. Further, other natural fibers can also be used in the present invention, such as abaca, sabai grass, milkweed floss, pineapple leaf, and the like. In addition, synthetic fibers can also be utilized, so long as such fibers do not have a substantial affect on the absorbency of the resulting tissue product. Some suitable synthetic fibers can include, but are not limited to, rayon fibers, ethylene vinyl alcohol copolymer fibers, polyolefin fibers, polyesters, and the like.

The paper product can also generally be formed by any of a variety of papermaking processes known in the art. In particular, any process capable of forming a paper web can be utilized in the present invention. For example, a papermaking process of the present invention can utilize adhesive creping, wet creping, double creping, embossing, wet-pressing,

air pressing, through-air drying, creped through-air drying, uncreped through-drying, as well as other steps in forming the paper web. Some examples of such techniques are disclosed in U.S. Patent Nos. 5,048,589 to Cook, et al.; 5,399,412 to Sudall, et al.; 5,129,988 to Farrington, Jr.; 5,494,554 to Edwards, et al.; which are incorporated herein in their entirety by reference thereto for all purposes.

In this regard, referring to Figure 1, one embodiment of a papermaking process that can be used for forming a paper web that is applied with a reactive composition of the present invention is illustrated. For example, the reactive composition can be a reactive, softening composition, such as set forth in Formula 2 above. Moreover, for simplicity, the various tensioning rolls schematically used to define the several fabric runs are shown but not numbered. Initially, a fibrous material is placed in a conventional paper making fiber stock prep beater or pulper (not shown) containing a liquid, such as water. If the fibers are cellulosic in nature, for example, the fibers may be refined in the beater or pulper until they become hydrated with the water. The fibrous material stock is typically kept in continued agitation such that it forms a liquid suspension can be formed.

In some embodiments, the reactive composition of the present invention may be combined with the fibers after and/or as the liquid suspension is formed within the pulper. After being intermixed, optionally with the reactive composition, the fibrous suspension can then be diluted and readied for formation into a layer of fibrous web using conventional papermaking techniques. In this regard, the fibrous suspension (i.e., stock slurry) may be stored in any apparatus, such as in a machine chest (not shown), prior to forming the web. In some embodiments, the reactive composition can also be combined with the fibrous material at the machine chest, prior to forming the web. If desired, the pH of the stock

slurry can also be adjusted for equipment compatibility.

As shown, a papermaking headbox 10 can then be used to inject or deposit a stream 11 of an aqueous suspension of papermaking fibers onto the forming fabric 12. The headbox 10 may be any web-forming headbox used in the art, such as a stratified headbox capable of producing a multilayered web. For example, it may be desirable to provide relatively short or straight fibers in one layer of the web to give a layer with high capillary pressure, while the other layer comprises relatively longer, bulkier, or more curled fibers for high permeability and high absorbent capacity and high pore volume. It may also be desirable to apply different chemical agents to separate layers of a single web to optimize dry and wet strength, pore space, wetting angle, appearance, or other properties of a web. Further, multiple headboxes may be used to create a layered structure, as is known in the art.

In some embodiments, the reactive composition can be added to the fibrous material at the headbox. For example, the reactive composition can be injected into the liquid suspension stream 11 just prior to entering the headbox 10. Moreover, when incorporated into a paper web having multiple layers, the reactive composition can generally be incorporated into any of the layers, either alone or in combination with cellulosic fibers. For example, in one embodiment, one of the layers can contain a mixture of the reactive composition and a cellulosic fibrous material. In another embodiment, a multi-layered paper web can also be provided that includes one layer of the reactive composition contained between layers of cellulosic fibers. It should be understood that a multi-layered paper web, such as described above, can be formed without using stratified or multiple headboxes, and can generally be formed according to any process known in the art.

From the stock-preparation stage, the fibrous slurry can then be



transferred to the web-forming stage. For example, in one embodiment, with the aid of a roll 14, the fibrous stream 11 can then be transferred to a fabric 13, which serves to support and carry the newly-formed wet web 15 downstream in the process as the web 15 is partially dewatered to a consistency of about 10 dry weight percent. Additional dewatering of the wet web 15 can be carried out, such as by vacuum suction, while the wet web 15 is supported by the forming fabric 13.

The wet web 15 is then transferred from the fabric 13 to a transfer fabric 17, which typically travels at a slower speed than the fabric 13 in order to impart increased stretch into the web 15. This is commonly referred to as "rush" transfer. One useful method of performing rush transfer is taught in U.S. Pat. No. 5,667,636 to Engel et al., which is incorporated herein in its entirety by reference thereto for all purposes. The relative speed difference between the two fabrics can be from 0% to about 80%, particularly greater than about 10%, more particularly from about 10% to about 60%, and most particularly from about 10% to about 40%. Transfer may be carried out with the assistance of a vacuum shoe 18 such that the forming fabric 13 and the transfer fabric 17 simultaneously converge and diverge at the leading edge of the vacuum slot 18.

Thereafter, any of a variety of papermaking techniques, such as drying, creping, embossing, etc., can be utilized. For example, the fibrous web 15 can be dried. Drying processes that incorporate infra-red radiation, Yankee dryers, through-air dryers, vacuum dewatering, microwaves, ultrasonic energy, etc., can be used. Thermal post-treatments can be further be used, alone or in combination with drying, to fuse a portion of any thermally fusible fibers that may be present in the material. As will be described in more detail below, in some embodiments, drying can cause the formation of covalent bonds between

any previously applied reactive composition and cellulosic fibers.

As shown in Fig. 1, in one embodiment, the web 15 is transferred from the transfer fabric 17 to a through-drying fabric 19 with the aid of a vacuum transfer roll or shoe 20. The through-drying fabric 19 can be traveling at about the same speed or a different speed relative to the transfer fabric 17. For example, if desired, the through-drying fabric 19 can run at a slower speed to further enhance stretch. The vacuum transfer roll or shoe 20 (negative pressure) can be supplemented or replaced by the use of positive pressure from the opposite side of the web 15 to blow the web 15 onto the next fabric.

The through-dryer 21 can accomplish the removal of moisture from the web 15 by passing air through the web without applying any mechanical pressure, i.e., non-compressive drying. Non-compressive drying can also increase the bulk and softness of the web. In one embodiment, for example, the through-dryer 21 can contain a rotatable, perforated cylinder and a hood (not shown) for receiving hot air blown through perforations of the cylinder as through-drying fabric 19 carries the fibrous web 15 over the upper portion of the cylinder. The heated air is forced through the perforations in the cylinder of the through-dryer 21 and removes the remaining water from the fibrous web 15. The temperature of the air forced through the fibrous web 15 by the through-dryer 21 can vary, but is typically from about 300°F to about 600°F.

The dried web 23 can then be transported by a carrier fabric 22 to a reel 24, where it can be wound. An optional turning roll 26 or fabric 25 can be used to facilitate transfer of the web 23 from the carrier fabric 22 to the reel 24. Although not shown, reel calendering or subsequent off-line calendering can be used to improve the smoothness and softness of the web 23. Besides calendering, any of a variety of other finishing steps can also be utilized. For example, the web 23 may be brushed to provide a

uniform exterior appearance and/or certain tactile properties. The material can also be wet creped, dry creped, and/or mechanically softened via other methods to improve softness and hand. Such processes can be in-line prior to winding up the fabric onto a roll, or they can be off-line. Adhesive recreping can be further used to improve strength and bulk properties. In addition, printed finishes can be applied to improve aesthetics.

As indicated above, the reactive composition can be applied during one or multiple stages of a papermaking process. For example, in some embodiments, the reactive composition can be applied during the stock preparation stage (e.g., the pulper, machine chest, headbox, etc.). Furthermore, the reactive composition, in some embodiments, can also be applied to the web-forming stage of the papermaking process. The web-forming stage generally refers to steps of a papermaking process that occur after the fibers are deposited on the forming fabric or wire, and before the web is dried. For example, in one embodiment, the composition of the present invention may be applied to the wet web 15 as it is formed onto the forming fabric 12 or the fabric 13. For instance, in one embodiment, the reactive composition can be sprayed onto the wet web 15 utilizing any of a variety of known spraying techniques.

Moreover, in some embodiments, the reactive composition may additionally be applied at the drying stage and/or the converting stage of the papermaking process. The converting stage generally refers to any stage of the papermaking process that occurs after drying the web. Further, in one embodiment, the reactive composition can be metered onto the dried paper web 23 before winding onto a roll 24. In some embodiments, the composition can also be metered in between two or more plies of the web 23.

Thus, as described above, the reactive composition of the present

invention can be applied at various of stages in a papermaking process. Moreover, depending on the particular stage in which the reactive composition is applied, it can sometimes have different effects on the resulting paper product. For instance, when the reactive composition is applied to the stock preparation stage and/or web-formation stage, such as described above, it is believed that the charged functionality of the composition initially forms an ionic bond with a charged group located on a cellulosic fiber, such as a carboxyl group. Thereafter, such as when the web is dried, it is believed that the covalent bonding functionality of the reactive composition forms a covalent bond with a free reactive group located on another cellulosic fiber within the paper web. However, it should also be understood that, in some instances, covalent bonds may preferentially form before the ionic bonds. Moreover, in some instances, a portion of the reactive composition may form an ionic and covalent bond with the same fiber. Nevertheless, it is believed that irregardless of the particular mechanism of bond formation, the reactive composition of the present invention will typically form an ionic bond with one cellulosic fiber and a covalent bond with an adjacent cellulosic fiber.

In this manner, a reactive composition of the present invention that has softening capabilities, for example, can soften the particular layer of the web to which it is added, and also inhibit lint and slough by forming a covalent bond with a reactive group located on the adjacent cellulosic fiber, such as free carboxyl groups.

Furthermore, as indicated above, the reactive composition can also be incorporated into a multi-layered paper web and/or into a multi-ply paper product during any stage of the papermaking process. For example, in some embodiments, the reactive composition can be applied to the surface of a first layer (e.g., outer or inner layer) of a multi-layered paper web at the converting stage of the papermaking process. For

example, in one embodiment, the reactive composition is applied to the outer surface of the inner layer of a three-layered paper web such that the treated surface is placed adjacent to an untreated surface of an outer layer of the web. Moreover, in another embodiment, the reactive composition is applied to the outer surface of the inner ply of a three-ply paper product such that the treated surface is placed adjacent to an untreated surface of an outer ply of the paper product.

When applied to a multi-layered web and/or multi-ply paper product, such as described above, it is believed that the covalent bonding functionality of the reactive composition allows it to bond to a cellulosic fiber within the layer while the softening moieties of the reactive composition, for example, debond the fibers of the layer for softening the layer. Thereafter, the treated layer can be placed adjacent to a second layer. In this embodiment, due to the action of the debonding groups on the treated layer, it is likely that very little ionic charge will remain for further reaction. The layer adjacent to the treated layer, in contrast, may have more charged groups, such as carboxyl groups, available for ionic bonding. Thus, the charged functionality of the reactive composition will preferentially form ionic bonds with carboxyl groups in the adjacent layer. As indicated above, it should also be understood that the ionic bonds may preferentially form before the covalent bonds. Moreover, in some instances, a portion of the reactive composition may form an ionic and covalent bond with the same fiber or within the same layer.

In this manner, a reactive composition of the present invention that has softening capabilities, for example, can soften the particular layer of the web to which it is added, and also inhibit lint and slough by forming a covalent bond with a reactive group located on the adjacent cellulosic fiber, such as free carboxyl groups, and also an ionic bond with a charged group on the cellulosic fibers, such as an anionically charged carboxyl

group.

Depending on the desired characteristics of the resulting paper product, the reactive composition of the present invention can also be utilized in varying amounts. For example, in some embodiments, the reactive composition can be applied in amounts up to 35 pounds per metric ton (lb/MT) of total fibrous material within a given layer, in some embodiments between about 1 lb/MT to about 10 lb/MT, and in some embodiments, between about 2 lb/MT to about 8 lb/MT.

Besides the reactive composition, additional chemical treatments can also be utilized at any stage of the papermaking process. For example, application of liquid treatments such as dyes, wet-strength agents, binders, brighteners, flame retardants, germicides, softening agents, starches, corrosion inhibitors, textile finishes, citric acid, ethylene diamine, etc., can be accomplished using spraying, dipping, squeeze techniques, vacuum extraction, liquid curtains, saturation techniques, and the like.

For example, in order to strengthen the tissue, various wet-strength agents can be applied in accordance with the present invention. Particular wet-strength agents that may be used in the present invention include latex compositions, such as acrylates, vinyl acetates, vinyl chlorides, and methacrylates. Other wet-strength agents may also be used including polyacrylamides (e.g., glyoxylated polyacrylamides), polyvinyl alcohols, and carboxymethyl cellulose. In one embodiment, the strength agent can be PAE resins, which are wet-strength agents that include polyamine-epichlorohydrin, polyamide-epichlorohydrin, polyamide-amine epichlorohydrin, and the like. These materials are sold by Hercules, Inc., Wilmington, Del., as "Kymene" (e.g. Kymene 557H or Kymene 557LX) and are believed to be described in U.S. Patent Nos. 3,700,623 and 3,772,076 to Keim, which are incorporated herein in their

entirety by reference thereto for all purposes.

Besides the above-mentioned materials, it should be understood that any other additive, agent, or material can be added to a paper product of the present invention, if desired. For example, additional additives are described in U.S. Patent Nos. 5,814,188 to Vinson, et al. and 5,830,317 to Vinson et al., which are incorporated herein in their entirety by reference thereto.

While the invention has been described in detail with respect to the specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.